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The influence of chemical composition and microstructure of API linepipe steels on hydrogen induced cracking and sulfide stress corrosion cracking

Rogério Augusto Carneiro [a], Rajindra Clement Ratnapuli [a], Vanessa de Freitas Cunha Lins [b,*]

[a] Research and Development Center, USIMINAS Steelworks, BR 381 Km 210, Zip code 35160-900 Ipatinga, MG, Brazil
[b] Chemical Engineering Department, Universidade Federal de Minas Gerais, Rua Espírito Santo 35, Zip code 30160-030 Belo Horizonte, Minas Gerais, Brazil

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Abstract

The chemical composition and microstructure are known to have a significant effect on the resistance to hydrogen induced cracking (HIC) and sulfide stress corrosion cracking (SSCC) of structural steels in wet H_2S environments. In this paper, the influence of microstructure on HIC and SSCC behavior of two low C–Mn–Nb–Mo API linepipe steels has been investigated. Subjecting the steel to different thermomechanical processes modified the microstructure. The results showed that refined and homogeneous quenched and tempered bainite/martensite microstructures had the best performance with respect to both HIC and SSCC susceptibility.

Keywords: Low alloy steel; Microstructure; Hydrogen embrittlement; Sulfide cracking

1. Introduction

Petroleum and natural gas systems contaminated with aqueous H_2S are very aggressive to the steels used in the transport and processing of these products. Inspection programs indicate that 25% of equipment failures in the petroleum refining industry are in some way associated with hydrogen damage [1]. The reaction between wet H_2S and the steel generates atomic hydrogen, a part of which gets absorbed into the steel. In the absence of applied stress, the diffused hydrogen could cause blistering or hydrogen induced cracking (HIC) initiated at hard phase constituents and non-metallic inclusions [2]. In the presence of applied stress and residual stress, the failure process can occur either by sulfide stress corrosion cracking (SSCC) through hydrogen embrittlement or stress oriented hydrogen induced cracking (SOHIC). The latter occurs mainly in lower strength steels, such as API linepipe grades.

Addition of a corrosion inhibitor, gas dehumidification or internal coating of linepipe steels may be done to prevent corrosion. But these procedures are often very expensive and difficult to execute. Attention has, therefore, been focused on developing suitable steels capable of resisting HIC and SSCC [3]. The production of these steels require adequate steel chemistries, special steel making and hot rolling practices aimed at improving cleanliness, reduce centerline segregation and obtaining a homogeneous microstructure.

This work evaluates the effect of chemical composition and microstructure of low C–Mn–Nb–Mo API linepipe steels on HIC resistance and stress corrosion cracking susceptibility in wet H_2S environments.

* Corresponding author. Fax: +55-31-3238-1789.
E-mail addresses: racarneiro@usiminas.com.br (R.A. Carneiro), vlins@deq.ufmg.br (V. de Freitas Cunha Lins).

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2. Experimental procedure

The steel was melted in a 50 kg vacuum induction furnace and cast into ingots of size 135 × 135 × 350 mm. The ingots were heated to 1250 °C for 180 min and rolled to 12.7 mm thick plates, using a controlled rolling process. The 63 mm thick intermediate slabs were rolled from 860 °C to a finish rolling temperature of 760 °C. Each plate was cut into three sections. One of the sections was normalized by heating to 900 °C for 60 min and cooling in air, and another was heated to 900 °C for 60 min and quenched in water, followed by a tempering heat treatment at 640 °C for 60 min. The third section was evaluated in the as rolled condition.

Metallographic sections were examined in a through-thickness plane parallel to the rolling direction, using optical and scanning electron microscopy (SEM). Tensile properties were obtained on transverse cylindrical specimens (10 mm in diameter and 50 mm gauge in length), conforming to the DIN standard (50125). Transverse Charpy impact specimens of size 10 × 10 × 55 mm, 2 V were tested at −20 °C according to ASTM E 23 standard.

HIC tests were performed according to the NACE standard, TM0284-96, which describes a methodology, used in the evaluation of HIC susceptibility of steels. Standard HIC samples (3 per plate) of 11 mm thickness, 20 mm width, and 100 mm length were tested in two different solutions saturated with H_2S. One used a pH of 3.5 (solution A) and the other a pH of 5.0 (solution B) as per NACE standard. These steel samples were taken along the rolling direction. Samples were polished to a 320 mesh, degreased and immersed in the test solutions. After the tests (72 h duration) the samples were examined for internal discontinuities using ultra sound C-Scan. This auxiliary analysis furnished additional information about crack distribution in the sample. However, the extent of HIC was quantified subsequently through metallographic analysis as specified in the standard. The transverse section of the samples was evaluated, and the HIC susceptibility was expressed using the following parameters (Eqs. (1)–(3)), defined in relation to crack length (a), crack thickness (b), sample width (w) and sample thickness (t): crack susceptibility ratio (CSR), crack length ratio (CLR), crack thickness ratio (CTR), and extension transverse crack (ETC), which is the maximum crack thickness.

$$\mathrm{CSR} = [(\Sigma\, a \cdot b)/w \cdot t] \cdot 100 \tag{1}$$

$$\mathrm{CLR} = [(\Sigma\, a)/w] \cdot 100 \tag{2}$$

$$\mathrm{CTR} = [(\Sigma\, b)/w] \cdot 100 \tag{3}$$

Stress corrosion cracking resistance was evaluated as per NACE TM 0177-96 method A using cylindrical test piece and a load ring. SSCC susceptibility was expressed by a threshold (or critical) stress, which is the maximum stress at which the sample survived 720 h of testing without fracture. The applied stress was varied from 50 to 100% of the yield strength (YS) of the material. Three samples were tested at each stress level.

3. Results and discussion

Table 1 shows the chemical composition of the two steels. Steel 2 had lower C and Si contents than steel 1. The low S and O contents of the steels combined with Ca treatment ensured high steel cleanliness and complete control of non-metallic inclusion morphology. The non-metallic inclusions consisted mainly of globular oxides (Ca-oxysulfides) and a small quantity of aluminum oxide.

The mechanical properties of the steels are listed in Table 2. For a given heat treatment the YS and tensile strength (TS) values of steel 1 were consistently higher than those of steel 2. This can be attributed to the higher C content and carbon equivalent value of steel 1. On the other hand the Charpy impact energy values of steel 1 were lower than those obtained in steel 2. In the controlled condition both steels are candidate materials for API-5L-X60 grade pipe.

Fig. 1 shows the microstructures of heat-treated plates of steel 1. In the controlled rolled condition the microstructure consisted of 79% ferrite (a mixture of deformed ferrite and polygonal ferrite), 21% pearlite and about 1% martensite–austenite. After normalizing the microstructure contained 82% polygonal ferrite, 13% pearlite and 5% austenite–martensite. The quenched and tempered plate was characterized by a homogeneous microstructure composed of 100% bainite/martensite. The microstructures of steel 2 are presented in Fig. 2. Here the controlled rolled plate showed 95% ferrite (mixture of deformed ferrite and polygonal ferrite), 3% pearlite and 2% martensite–austenite. Normalizing resulted in a structure containing 94% polygonal ferrite, 3% pearlite and 3% austenite–martensite. Interestingly, because of the lower harden ability of steel 2 the quenched and tempered microstructure consisted basically of a ferrite (96%)–pearlite (4%) structure. The deformed ferrite observed in the controlled rolled material of both steels may be attributed to the fact that finish-rolling temperatures of the two steels were below the Ar_3 temperatures (750/770 °C). A part of the finish rolling of these two steels had in effect been carried out in the austenite plus ferrite region.

HIC test results are listed in Table 3 for pH of 5.0 and in Table 4 for pH of 3.5. Independent of the thermomechanical treatment, steel 1 was found to be free from internal cracks when tested both by ultra sound inspection and metallographic analysis (Table 3). In the case of steel 2 ultra sound C-scan revealed internal discontinuities in HIC coupons taken from the as rolled as well

Table 1
Chemical composition of the steels

Steel	Chemical composition (wt.%)														
	C	Si	Mn	P	S	Al	Ni	Cu	Cr	Nb	V	Mo	Ca	N	O
API Stand.	0.26 (max)	–	1.40 (max)	0.040 (max)	0.050 (max)	–	–	–	–	0.005 (max)	0.02 (max)	–	–	–	–
1	0.09	0.26	0.82	0.010	0.0025	0.025	0.20	0.39	0.021	0.039	0.060	0.30	0.005	0.002	0.002
2	0.035	0.12	0.87	0.013	0.0035	0.043	0.14	0.30	0.005	0.031	0.056	0.31	0.004	0.001	0.002

Table 2
Mechanical properties of the steels

Heat treatment	Yield strength YS (MPa)	Tensile strength TS (MPa)	% Elongation (50 mm)	Hardness HV (5 Kgf)	Charpy (J) 0 °C	Impact (J) −20 °C	Transverse (J) −40 °C
1R	473	589	25	232	174	155	122
1N	293	504	34	161	300	262	144
1QT	616	682	20	243	262	244	229
2R	464	550	29	193	> 300	> 300	> 300
2N	259	440	39	153	> 300	> 300	> 300
2QT	512	578	22	162	> 300	> 300	> 300

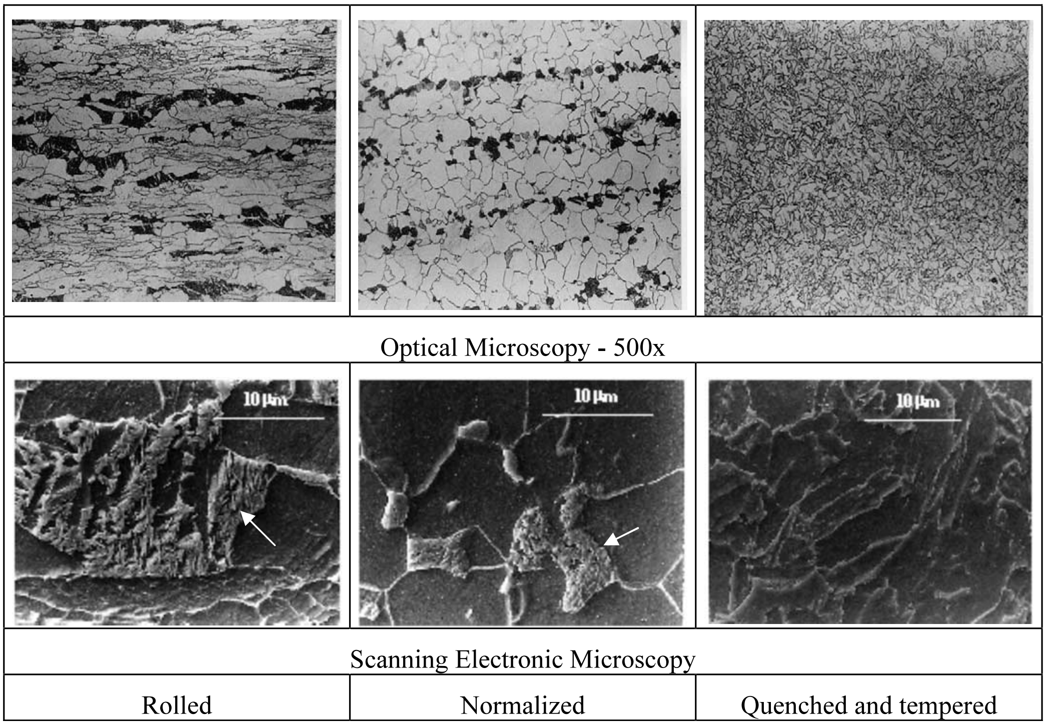

Fig. 1. Microstructures of steel 1 after thermomechanical processing. The arrows in the SEM micrographs and the dark areas in the OM micrographs indicate the pearlite.

as quenched and tempered plates. However, when the cracks were analyzed metallographically according to the NACE TM0284-96 standard steel 2 was found to be free of cracks. These results are in accordance with published data, which show that copper additions in the order of 0.30% tend to improve HIC resistance of steels exposed to wet H_2S environments with pH of 5.0 [4]. The copper promotes the formation of a protective surface film of the type (FeCu)·S on the steel, which retards the hydrogen generation reaction.

As shown in Table 4, in low pH solutions only the quenched and tempered plate of steel 1 survived the HIC

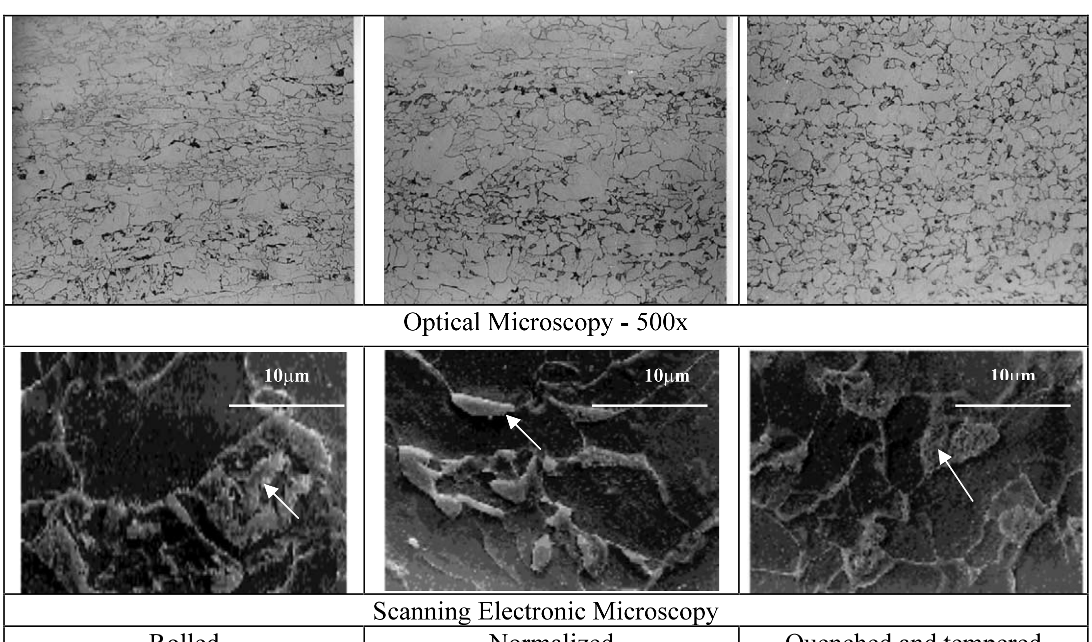

Fig. 2. Microstructures of steel 2 after thermomechanical processing. The arrows in the SEM micrographs and the dark areas in the OM micrographs indicate the pearlite.

Table 3
Results of HIC test in solution with pH 5.0

Steel	Ultra-sound	CLR_{max} (%)	CLR_{med} (%)	CTR (%)	CSR (%)	ETC (mm)
1R	No cracks	0	0	0	0	0
1N	No cracks	0	0	0	0	0
1QT	No cracks	0	0	0	0	0
2R	Cracks	0	0	0	0	0
2N	No cracks	0	0	0	0	0
2QT	Cracks	0	0	0	0	0

test without cracking. This steel had a homogeneous and refined tempered bainite/martensite microstructure.

Table 5 shows the values of the threshold stress, as a percentage of the YS, which are obtained after the stress corrosion tests. The threshold stress of the quenched and tempered steel with 0.09% C is 85% of the yield stress, which is higher than the critical value of the other tested samples. The improved SSCC resistance of the quenched and tempered plate of this steel can be attributed to its homogeneous bainite/martensite microstructure, which made the crack propagation difficult [5–7]. Albarran et al. [3] observed that quenching and tempering provides an optimum SSCC resistance of the API X-80 steels as the applied intensity factors had to be raised to 40 MPa $m^{-1/2}$ before crack propagation could be observed. For the quenched and tempered steel with a carbon content of 0.035%, the critical stress amounted to 70% of the YS, which is the same as that obtained for the normalized plate but much higher than that of the as rolled plate. On the basis of the nominal applied stress, the quenched and tempered steel gave the highest critical stress. The deformed analysis of cracked SSCC test specimens showed that in general, the cracks nucleated both from surface imperfections or pits and from internal HIC. Fig. 3 shows the surface of fractured steel with 0.035% C, after 12 h of corrosion testing according to NACE TM 0177-96 method A standard. The applied stress was 100% of the YS of the steel. HIC and a corrosion pit can be observed. Stress corrosion cracks can initiate at pits that form during exposure to service environment or by prior cleaning operations. Fig. 4 presents transverse sections of steel 2, after 12 h of the stress corrosion test. The applied stress was 100% of the YS of steel. Fig. 4 shows cracks that nucleated from surface imperfections. HIC can be seen in transverse sections of steel 2. The HIC cracks propagated in a direction parallel to the stress direction. The application of tensile stress increased the internal stress in the area surrounding the HIC cracks and generated localized yielding, which produced a second crack perpendicular to the tensile stress direction. Stress field of these cracks generated deformation bands, which joined the crack edges. Small HIC cracks were nucleated in the deformation bands. These small cracks coalesced and joined the two HIC. The repetition of this process produced the failure by stress corrosion, which occurs as a SOHIC process, according to Takahashi and Ogawa [8], and Miranda [9]. The same fracture morphology was obtained for the steel 1.

Table 5
Test time (h) for fracture in stress corrosion tests

Steel	Applied stress (% Yield strength of steel)				
	100	85	70	60	50
1R	4	18	720	–	–
1N	19	28	632	720	–
1QT	8	720	–	–	–
2R	7	114	365	720	–
2N	18	212	720	–	–
2QT	22	28	720	–	–

Table 4
Results of HIC test in solution with pH 3.5

Steel	Ultra-sound	CLR_{max} (%)	CLR_{med} (%)	CTR (%)	CSR (%)	ETC (mm)
1R	Cracks	10.2	3.4	3.1	0.3	0.34
1N	Cracks	11.9	7.7	3.3	0.4	0.36
1QT	No cracks	0	0	0	0	0
2R	Cracks	12.7	11.5	4.0	0.4	0.45
2N	Cracks	8.2	3.4	1.6	0.1	0.12
2QT	Cracks	10.7	3.6	3.7	0.4	0.42

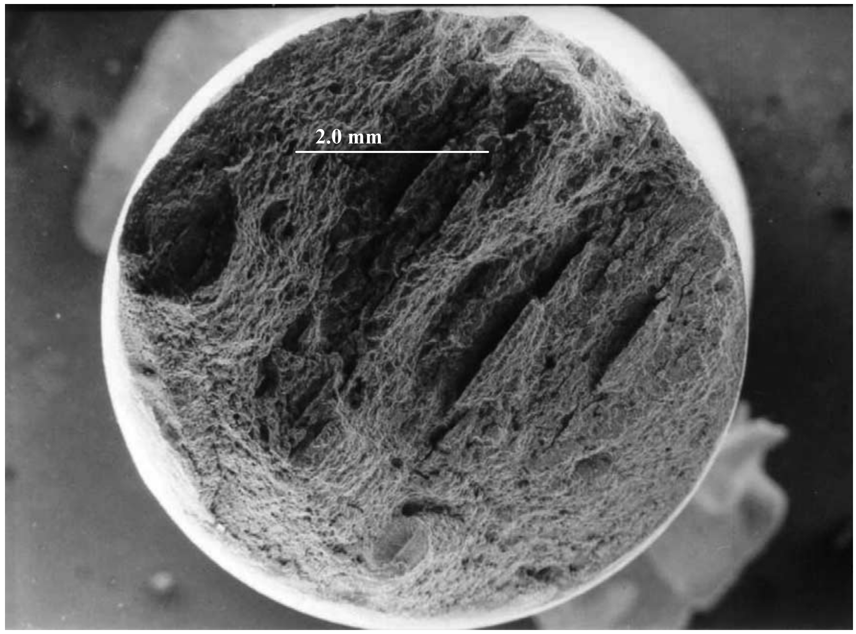

Fig. 3. Surface of fractured steel with 0.035% C, after 12 h of corrosion testing according to NACE TM 0177-96 method A standard. The applied stress was 100% of the YS of the steel.

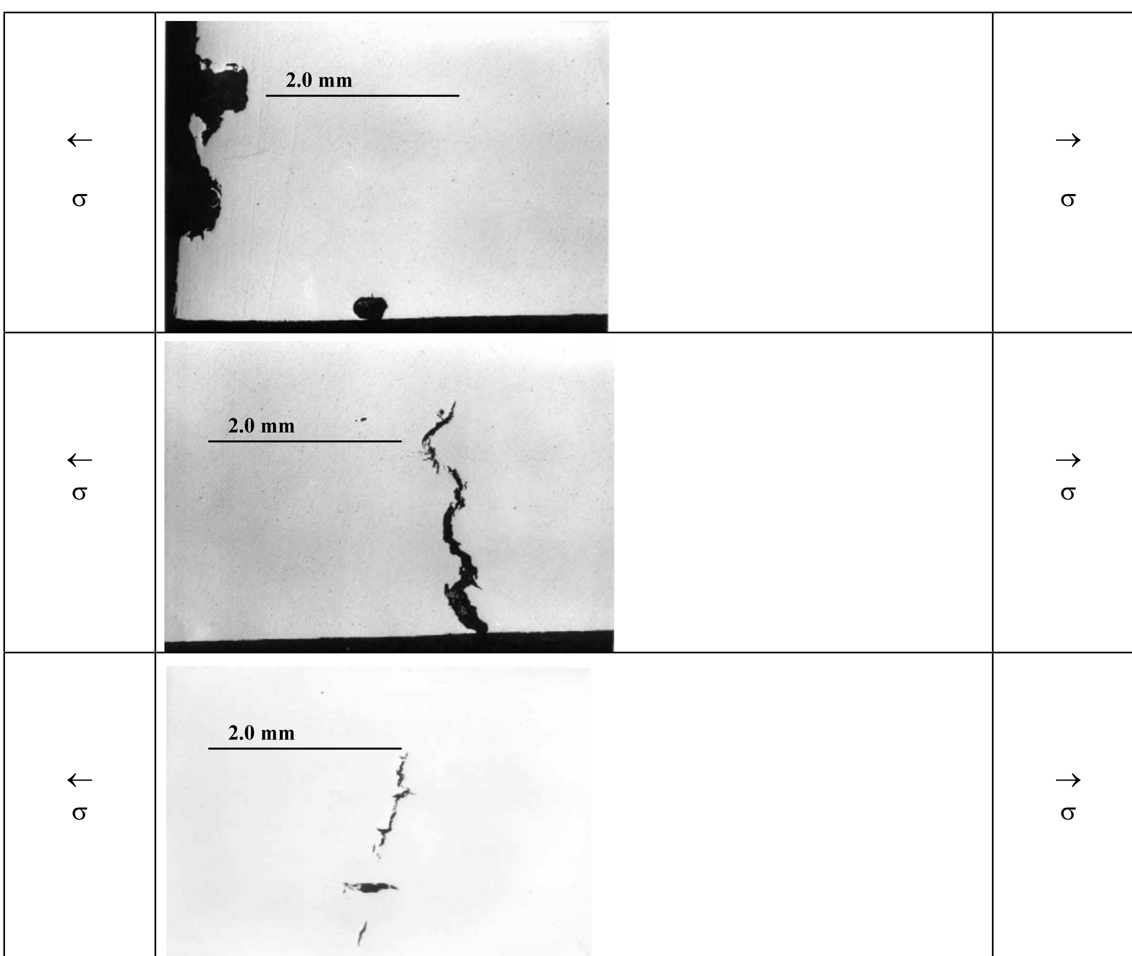

Fig. 4. Transverse sections of steel 2, after 12 h of the stress corrosion test. The applied stress was 100% of the YS of steel.

4. Conclusions

A refined homogeneous quenched and tempered bainite/martensite microstructure simultaneously improved HIC performance and SSCC resistance of the steels examined.

In general the rolled as well the normalized steels which contained ferritic–pearlitic microstructures showed greater susceptibility to SSCC. On the basis of the critical nominal applied stress, the SSCC resistance of the rolled steels was superior to the normalized steels.

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